Cation Exchange Finishing of Nonwoven Polyester with Polycarboxylic Acids and Cyclodextrins

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ABSTRACT: We describe a chemical method for the finishing of polyester nonwoven fabrics that aimed to obtain ion exchange textiles. This approach was based on the use of polycarboxylic acids (PCA) and cyclodextrins as carbohydrate compounds and finishing agents, respectively. It was observed that the reaction between these reactants yielded a crosslinked polymer that was physically anchored onto the fibers. This polymer can be considered as a resin issued from the esterification between the COOH groups of the PCA with the OH groups of the carbohydrate. As the esterification reaction was not complete, many free carboxylic groups remained on the surface of the coating polymer. This feature offered the ion exchange properties to the textile support. In this article, we described the pad-dry-cure process and showed the influence of the curing parameters (time and temperature), the nature, and the concentration of the components and the pH of the impregnating bath. The grafting rate (in wt %) and the ion exchange capacity (IEC) were observed in parallel. First, it was observed that the best IEC capacity (that could reach 1 mmol/g) was obtained when an ideal compromise was applied between time and temperature of curing. We also evidenced that IEC depended on the nature and on the concentration of the PCA (chosen among citric acid, 1,2,3,4-butanetetracarboxylic acid, and polyacrylic acid) and on the pH of the impregnating bath. Finally, it was observed that cyclodextrins were more appropriate than starch as finishing coreactants. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 103: 3730–3738, 2007

Key words: ion exchangers; polyester; textile finishing; cyclodextrins; polycarboxylic acids

INTRODUCTION

A large majority of the ion exchange systems are based on microporous resins for purification of water and separation of ionic compounds. Resins present the advantages of being stable and efficient.[1] In the last two decades, ion exchange textiles development has brought new properties and more advantages. Indeed, ion exchange textiles are stable and efficient, are easier to handle than resins, present a larger exchange-specific surface, and their structure presents a lower resistance to solution flow.[2] Some applications are developed or are thought again around ion exchange textiles: production of high-resistivity water for pharmaceutical and electronic industry, removal of heavy metal ions in wastewater.[2–6]

The purpose of this work was to obtain an efficient cation exchange textile from the grafting reaction of cyclodextrins (CDs) onto nonwoven supports made of polyethyleneterephthalate fibers. At the origin, this reaction was developed to graft CDs onto cotton, wool,[7] and polyester fabrics,[8] by using polycarboxylic acids (PCA) as crosslinking agents. This finishing reaction offered new properties to the textiles, as they present enhanced properties of sorption and controlled delivery of many organic molecules like fragrances[9] or aromatic pollutants,[10] through their inclusion into the grafted CD cavities.

Besides the molecular encapsulation properties of CDs, we recently observed that the presence of unesterified carboxylic groups in the polymeric structure made from CDs and PCA could also attribute ion exchange capacity (IEC) to the fibers. In fact, in 1981 Carrington and Hall already showed that it was possible to graft PCA onto cellulose fibers to prepare a carboxylated cellulose ion exchange material by heating a mixture of cellulose and PCA.[11] In the present article, we demonstrate that the use of CDs as coreactants with PCA permits to extend this method to polyester fabrics.

As presented in Scheme 1, the reaction occurs by a first dehydration of PCA, which yields a 5- or 6-membered cyclic anhydride intermediate that readily reacts with hydroxyl groups of CDs by esterification. Then, two of the remaining carboxylic groups of the reacted PCA can form a second anhydride that can also react with another CD. As CD presents many hydroxyl groups and thus may react with other PCA

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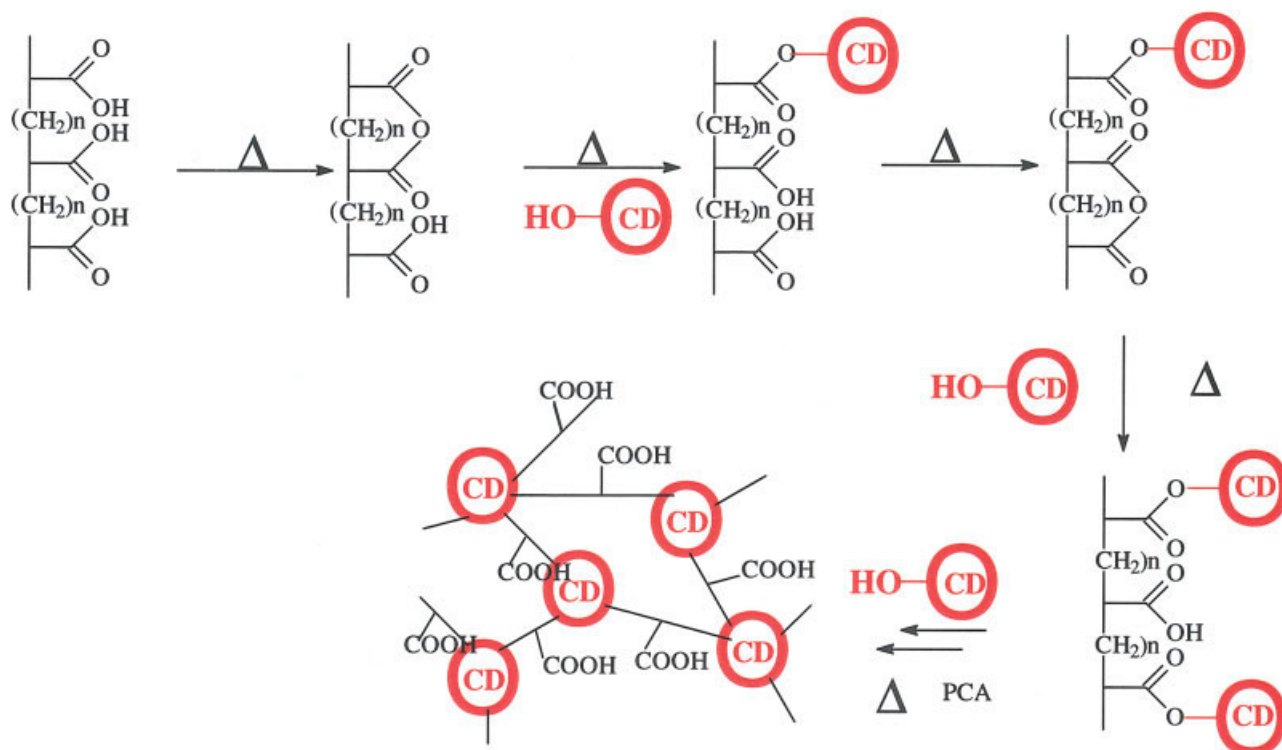
Scheme 1 Detail of the mechanism of esterification between a PCA and cyclodextrin. The reaction yields a crosslinked CD polymer with unreacted carboxylic groups. This polymer coats the polyester fibers that are transformed into ion exchange fibers. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

moieties, a polymerization can develop and a crosslinked polymer is formed *in situ*, in the fibrous network. The resulting polymer forms a coating of the fibers, as observed in Plate 1. The last step of the reaction scheme shows that some carboxylic functions of the PCA residues remain unreacted. So, the structure of the coating polymer includes CD moieties and numerous unreacted carboxylic groups resulting from the partial esterification of the PCA crosslinking agent.

The purpose of this article was to show that the unreacted COOH groups will give an important cation exchange capacity to the modified fabric support.

We present the study of the parameters involved in this finishing process and their influence on the grafting rate and the IEC. These parameters include curing time and temperature, the pH of the impregnation bath, the nature and concentration of the PCA (citric acid, 1,2,3,4-butanetetracarboxylic acid (BTCA), and polyacrylic acid (PAA)) and of the polysaccharides (starch, and CDs (α-CD, β-CD, γ-CD)), and the concentration of the catalyst.[12,13]

EXPERIMENTAL

Materials

Nonwoven polyester, supplied by Nordlys (PGI group, Bailleul, France) was used throughout the study. 1,2,3,4-Butanetetracarboxylic acid (BTCA), citric acid hydrate (CTR), polyacrylic acid (PAA, M_w = 2000), sodium hypophosphite (NaH$_2$PO$_2$), and calcium acetate were from Aldrich Chemicals (Milwaukee, WI). α-CD and γ-CD were supplied by Wacker Chemie GmbH (Cavamax®, Burghausen, Germany) and β-CD and starch were gifts from Roquette (Kleptose®, Lestrem, France).

The textile finishing equipment consisted of two-roll pad. The curing oven (Roaches, UK) is equipped with a mechanical circulation of air.

Methods

The nonwoven support was preliminarily washed by soxhlet (water was used as the solvent) to remove the auxiliaries. Before treatment, all fabrics were oven dried at 104°C for 1 h, placed into a desiccator for 30 min, and immediately weighed.

In standard conditions, 100 mL of the initial solution that was used to impregnate the fabric contained 10 g of one of the PCA (chosen among CTR, BTCA, and PAA), 1 g of the catalyst (NaH$_2$PO$_2$), and 10 g of CDs. In the study of the influence of the pH of the initial solution on the reaction, pH was adjusted to the desired value by addition of HCl (1M) or NaOH (1M). The fabric was then impregnated with this solution and padded. The wet pick
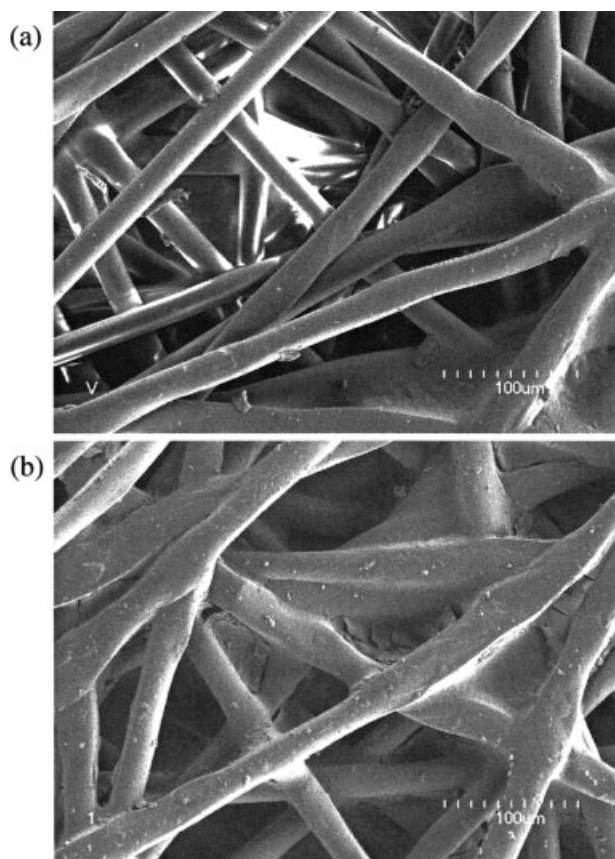
Plate 1 SEM of polyester untreated fibers (a) and coated by the crosslinked polymer formed between PCA and CD (b).

up was 100% ± 3%. The fabric was mounted on a pin frame and oven dried at 90°C for 6 min. Curing then occurred at the desired temperature (140 < T < 200°C) and time (1 < t < 60 min). Samples were washed again by soxhlet (water was used as the solvent) to remove unreacted products, oven dried (at 104°C), placed into a desiccator for 30 min, and weighed. The grafting rate (reported by wt %) was reported as the weight gain of the samples; and the following equation was used:

$$\% \; \text{wt} = \frac{m_f - m_i}{m_i} \times 100$$

where m_i and m_f are the weight of the sample before and after treatment, respectively. Precision of the value of wt % was estimated to be ±1.5%.

The IEC of each sample was determined by pH-metric titration[14] according to the method of calcium acetate described in the United States Pharmaco-

poeia (USP 1995). A calcium acetate solution (2% w/w) was prepared by solubilizing calcium acetate in distilled water. A sample of fabric (10 × 15 cm²) was dried in oven (104°C) for 1 h, placed in desiccator for 30 min, and weighed. The sample was broiled and placed into the calcium acetate solution for 4 h. The solution was filtered, and the amount of acetic acid formed was determined by pH-metric titration by using standardized sodium hydroxide solution (0.05M). The amount of ion exchange functions is equal to the amount of acetic acid in solution (Scheme 2). The results are reported in millimoles of COOH groups per gram of fabric.

RESULTS AND DISCUSSION

Influence of the curing parameters on the grafting rate

Figures 1(a), 1(b), 2(a), 2(b), 3(a), and 3(b) represent the evolution of the grafting rate against temperature (a) and time (b) of curing, for CTR, BTCA, and PAA, respectively.

In the case of the three PCAs, it was observed that the grafting rate increased with the temperature of curing [Figs. 1(a), 2(a), and 3(a)], and then stabilized at a maximal value. The plateau was reached at the lowest temperatures for longest curing times, and the curves overlapped above 20 min of curing.

In parallel, it was observed that the grafting rate increased with the time of curing [Figs. 1(b), 2(b), and 3(b)], and then stabilized at a maximal value. In the case of the three PCAs, the maximal grafting rate was comprised between 15 and 20 wt %.

The study of Figures 1(a), 1(b), 2(a), 2(b), 3(a), and 3(b) shows that the effects of curing time and curing temperature are intimately connected.

The data obtained from Figures 1(a), 1(b), 2(a), 2(b), 3(a), and 3(b) were combined together, to generate the two-dimensional graphs presented in Figures 1(c), 2(c), and 3(c). These graphs report the resulting grafting rate of the fabrics, in function of the time and of the temperature of curing. These figures clearly showed that the grafting rate increased with time and temperature parameters and allowed the setting the grafting conditions to obtain a desired grafting rate.

Influence of the curing parameters on the IEC

In parallel, the IEC of all samples studied in the aforementioned study was determined by titration

Scheme 2 Determination of the IEC by reaction of calcium exchange with carboxylic functions of treated polyester fabrics. Acetic acid formed is back titrated.
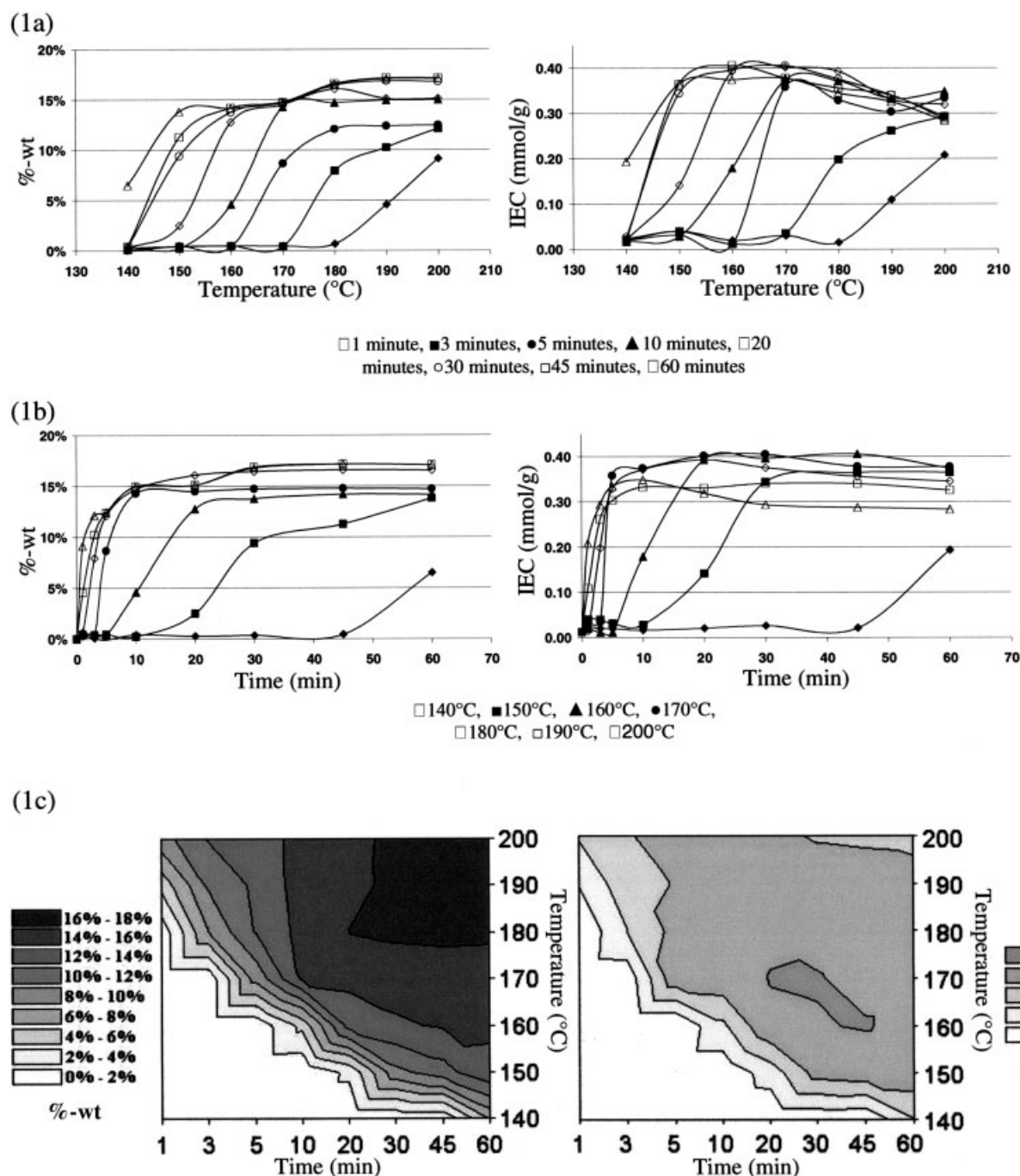
Figure 1 Effect of curing temperature (a) and curing time (b) on the weight gain (wt %) and IEC (mmol/g) of polyester fabrics grafted with CTR. (c) is a two-dimensional combined graph of (a) and (b) (formulation (10/1/10) (CTR/NaH$_2$PO$_2$/β-CD), pH = 2).

with calcium acetate. The variation of IEC could be observed in function of the curing parameters, i.e., temperature [Figs. 1, 2, and 3(a)] and time [Figs. 1, 2, and 3(b)], in the case of CTR, BTCA, and PAA, respectively. As applied in the study of the grafting rate, the data obtained from Figures 1, 2, 3(a), and 3(b) were combined together to generate the two-dimensional graphs presented in Figures 1, 2, and 3(c).

On the opposite of what was observed in the determination of the grafting rate of the samples, it is observed that the curves report the IEC versus time and temperature of curing presenting maximal IEC values for intermediary conditions of curing, and then a decrease.

At low values of time and temperature of curing, IEC evolved in a parallel way with regard to wt %.
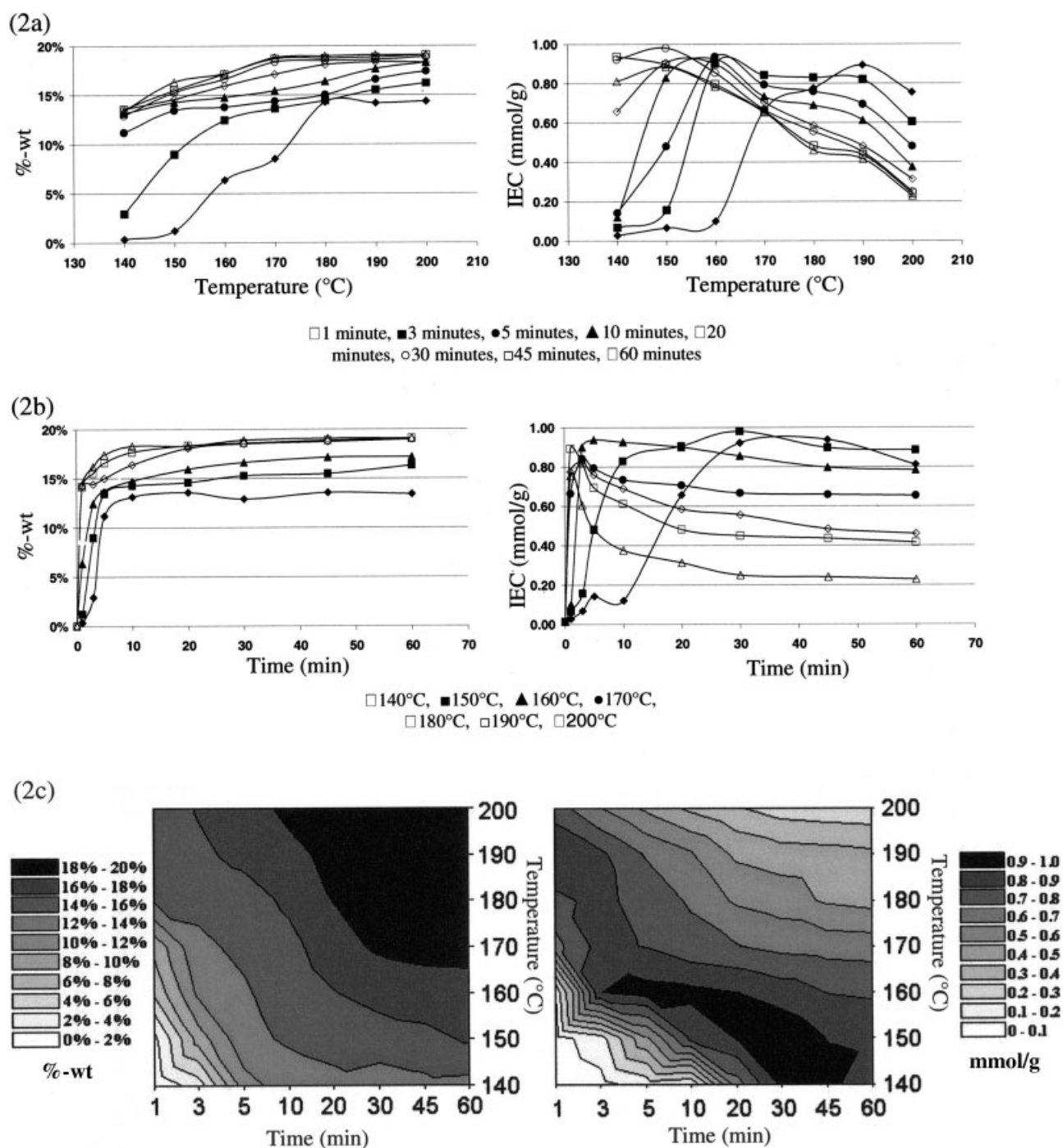
Figure 2 Effect of curing temperature (a) and curing time (b) on the weight gain (wt %) and IEC (mmol/g) of polyester fabrics grafted with BTCA. (c) is a two-dimensional combined graph of (a) and (b) (formulation (10/1/10) (BTCA/NaH$_2$PO$_2$/β-CD), pH = 2).

This is attributed to the development of the fixation of the crosslinked polymer formed between PCA and CD onto the support. It is observed that the fixation occurred from threshold values of time and temperature of curing.

For the highest values of time and temperature of curing applied, wt % reached a plateau value, while IEC decreased. This decrease of IEC under drastic

conditions is interpreted by a maximal rate of esterification that causes the disappearance of the free COOH groups present in the β-CD polymer structure.

In conclusion, the maximum of IEC of the fabrics corresponds to the best compromise between the grating rate, i.e., the amount of polymer fixed onto the fibers, and the crosslinking rate of the fixed polymer.
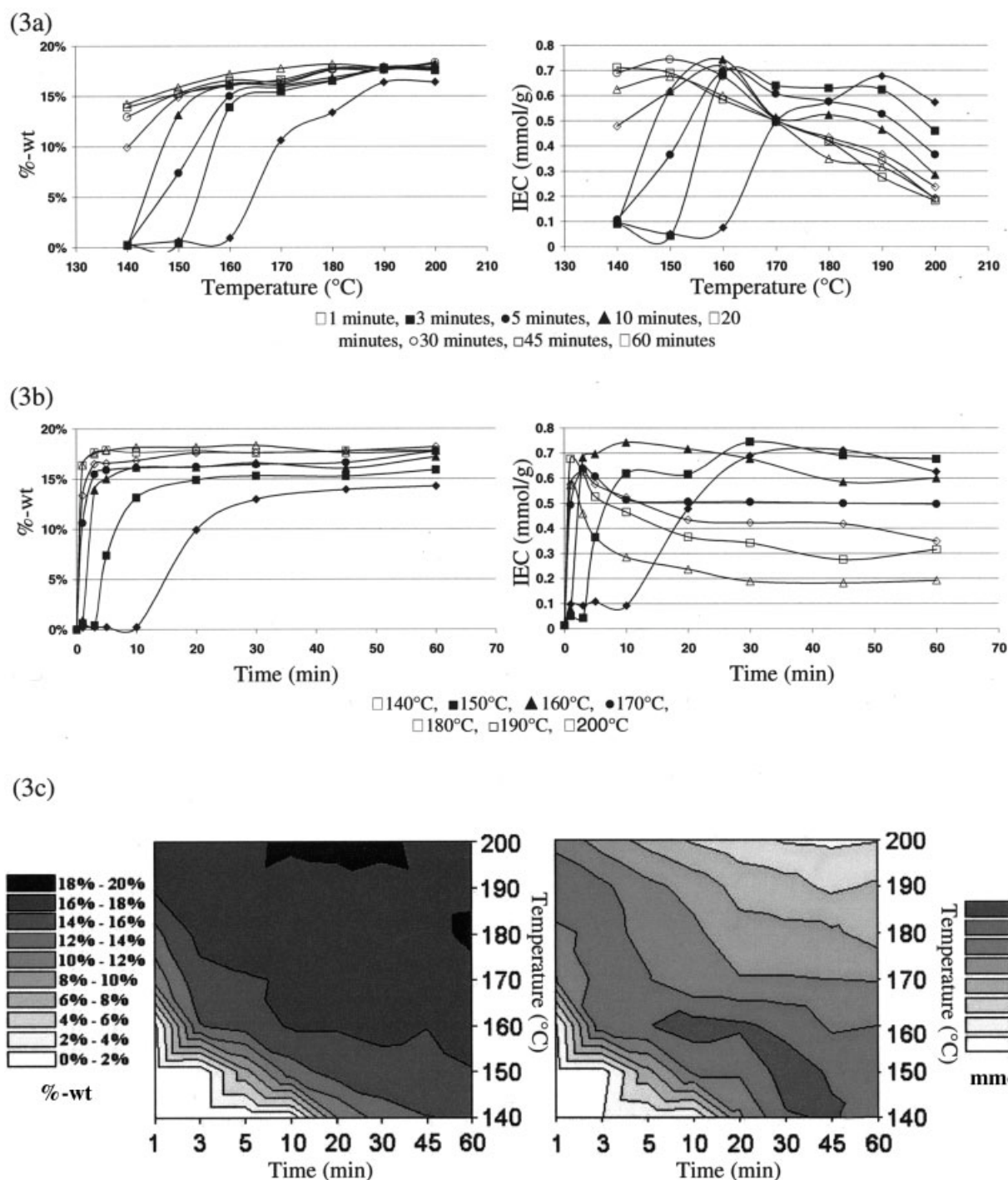
(3a)

(3b)

(3c)

Figure 3 Effect of curing temperature (a) and curing time (b) on the weight gain (wt %) and IEC (mmol/g) of polyester fabrics grafted with PAA. (c) is a two-dimensional combined graph of (a) and (b) (formulation (10/1/10) (PAA/NaH$_2$PO$_2$/β-CD), pH = 2).

Influence of the nature and of the concentration of the PCA

We varied the ratio PCA/β-CD in the initial solution, and observed the parallel evolution of the grafting rate and IEC at fixed curing parameters.

CTR and BTCA concentrations were varied in the range of 0–150 g/L, while that of PAA was limited to 100 g/L. β-CD concentration was fixed to 100 g/L.

The results presented in Figures 4(a) and 4(b) show that the grafting rate and IEC are dependent on the ratio of PCA introduced into the impregnating bath. Moreover, it is also observed that the IEC also depended on the nature of the PCA (BTCA > PAA > CTR).

Such differences can be explained by the difference of the chemical structure of the three PCAs,
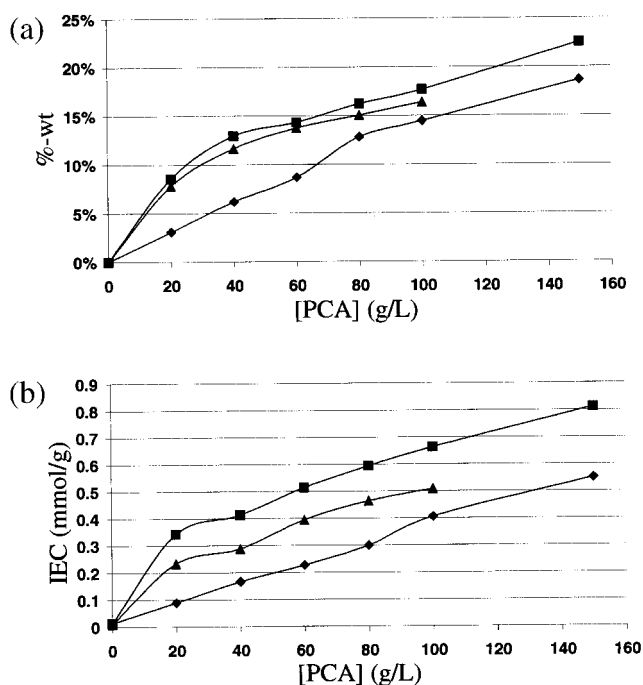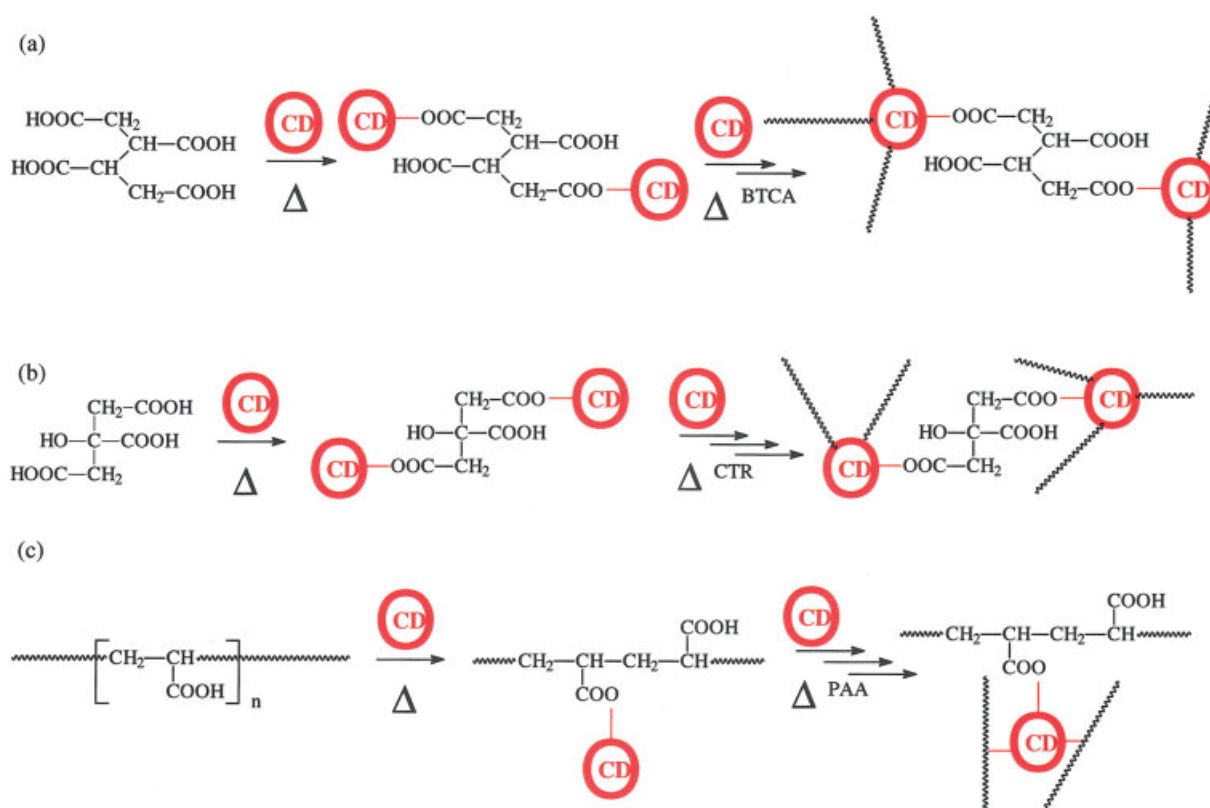
Figure 4 Increase in weight (a) and ion exchange capacity (b) of the polyester fabrics with concentration of PCA (CTR (♦), BTCA (■), PAA (▲); formulation $(x/1/10)$ (PCA/NaH$_2$PO$_2$/β-CD), $T = 170°C$, $t = 30$ min, pH = 2).

and by the structure of the resulting crosslinked polymeric structure. This is highlighted by the simplified reaction scheme observed in Schemes 3(a) and 3(c). The BTCA structure contains four carboxylic acid groups; after the esterification reaction with two β-CD units, it is observed that each BTCA unit included in the polymeric structure presents two residual carboxylic groups [Scheme 3 (a)]. CTR, which presents three carboxylic acid groups, presents only one residual carboxylic function in the polymeric structure [Scheme 3 (b)]. So it is possible to estimate that in the theoretical case, half of the carboxylic functions of BTCA remain free, while only one third of those of CTR are still present. This remark is in correlation with our results and explains why the IEC of BTCA-treated samples was higher than that of CTR.

Influence of the nature and of the concentration of polysaccharides

The next step of the study consisted of comparing three different native CDs which differ only by the number of glucopyranosic units involved in the CDs macrocycle, and starch that consists of the same repetition unit, but forming a linear macromolecule

Scheme 3 Simplified descriptions of the reaction between (a) BTCA, (b) CTR, and (c) PAA and cyclodextrin. In each case, one can observe the theoretical structure of the partially esterified PCA units in the resulting crosslinked polymer. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
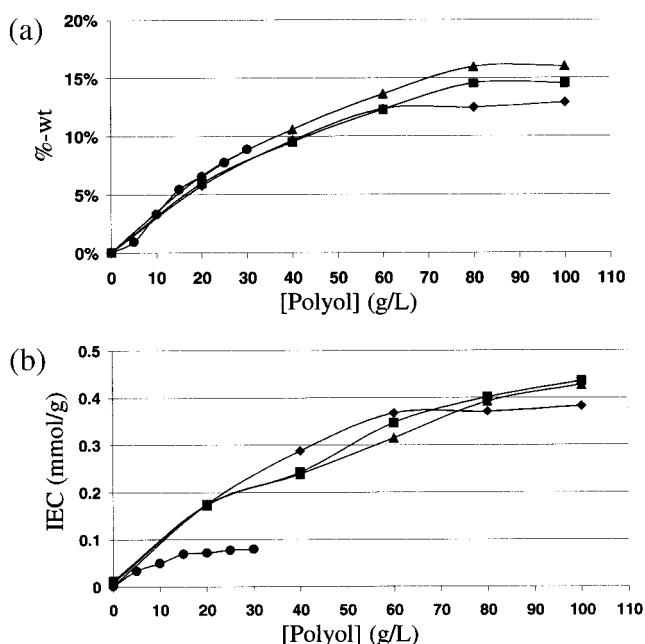
Figure 5 Increase in weight (a) and ion exchange capacity (b) of the polyester fabrics with concentration of polyol (α-CD (◆), β-CD (■), γ-CD (▲), starch (●); formulation (10/1/x) (CTR/NaH₂PO₂/polysaccharide), $T = 170°C$, $t = 30$ min, pH = 2).

with a higher molecular weight, and a solubility lower than that of CDs in the impregnating solution.

Figures 5(a) and 5(b) report the study of the variation of the grafting rate, and of the IEC versus the concentration of the polysaccharides mentioned above.

Figure 5(a) demonstrates that the nature of the polyols did not involve any difference in the grafting rates of the samples as an overlapping of the four curves is observed.

Figure 5(b) shows that, amazingly, the evolution of IEC of the three kinds of CDs-treated samples was similar, but that of the starch-treated samples was inferior. So, CDs are far more appropriate than starch in the frame of this study. This limitation for the use of starch was its solubility in the impregnation bath that was limited to 30 g/L (instead of 100 g/L in the case of CDs), and that the resulting crosslinked polymer formed between starch and CTR presented a lesser amount of carboxylic groups.

Influence of the catalyst concentration of the initial solution

Sodium hypophosphite is reported to be an appropriate catalyst in the case of the finishing of cotton fabrics with PCA, as reported by Welch.[15] Furthermore, more recently we also confirmed this tendency in the CDs finishing of cotton fabrics.[7]

Figures 6(a) and 6(b) report the influence of the concentration of sodium hypophosphite on the grafting rate and on the IEC of the samples, respectively.

It is observed that, contrarily to the treatment of cotton,[16] the presence of this catalyst only presents a low influence on the reaction in the case of polyester finishing. As a matter of fact, the surface modification was observed even in the absence of any catalyst. Though, an optimal concentration of 10 g/L provokes an increase in the range of 20% of the results, and confirmed the opportunity of the use of a catalyst in this reaction. Moreover, such an observation has been previously reported in the study of the synthesis of CD gels using the same chemical path.[17]

Influence of the pH of the impregnation bath

We varied the pH of the initial solutions by using HCl (1M) or NaOH (1M), in the presence and in absence of the catalyst (10 g/L) and we observed the grafting rate and IEC evolutions.

Figure 7 shows that pH values below 3 correspond to optimal conditions, while pH values over 4 (BTCA) and 5 (CTR and PAA) provoke the inhibition of the reaction.

This latter phenomenon is because pH values over 4 or 5 are superior to the pKa of the carboxylic groups and they correspond to the predominance of the carboxylate forms which were unfavorable to the
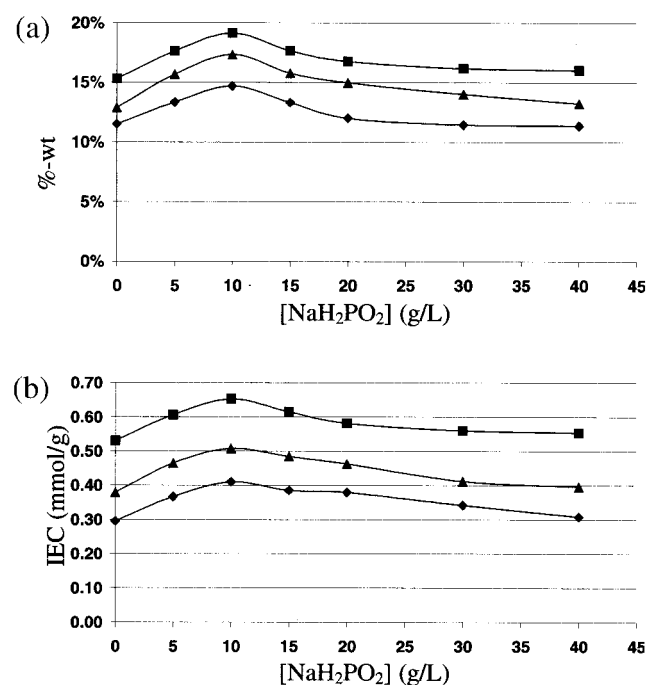

Figure 6 Increase in weight (a) and ion exchange capacity (b) of the polyester fabrics with concentration of NaH₂PO₂ (CTR (◆), BTCA (■), PAA (▲); formulation (10/x/10) (PCA/NaH₂PO₂/β-CD), $T = 170°C$, $t = 30$ min, pH = 2).
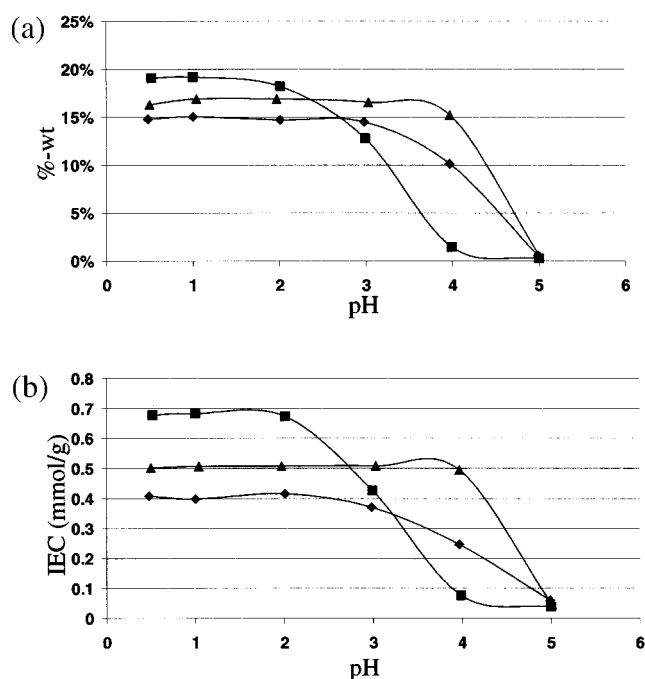
Figure 7 Increase in weight (a) and ion exchange capacity (b) of the polyester fabrics with pH, (CTR (◆), BTCA (■), PAA (▲); formulation (10/1/10) (PCA/NaH$_2$PO$_2$/β-CD), $T = 170°C$, $t = 30$ min).

formation of the intermediate cyclic anhydrides[18] that are involved in the reaction mechanism.

CONCLUSIONS

This article presented a convenient way to easily transform raw polyester fibers into ion exchange textiles, through a pad-dry-cure process. The reaction consisted of accomplishing a polyesterification between PCAs and CDs to form a functional cross-linked polymer coating the fibers. The IEC of the modified fibers was due to the existence of many unreacted carboxylic groups remaining in the structure of this coating polymer.

It was observed that optimal IEC values were obtained for intermediate curing parameters, as they resulted from the best compromise between the largest possible grafting rates, and the lowest possible degree of esterification of the carboxylic groups in the coating polymer.

We observed that CDs were convenient coreactants as they present a large amount of esterificable hydroxyl groups, and moreover, they presented a higher solubility than starch in the initial solution.

The best IEC values reached 1 mmol/g of carboxylic functions in the case of a treatment with BTCA, which is a value close from classical data present in the literature. The applications of these textiles will deal with the domain of the removal of metallic cations from waste waters and soils and will be reported soon.

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